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BUREAU OF MINES
HELIUM ACTIVITY
HELIUM RESEARCH CENTER
INTERNAL REPORT

THERMODYNAMIC PROPERTIES OF HELIUM FOR TEMPERATURES BETWEEN 0°
AND 150° C AND PRESSURES TO 300 ATMOSPHERES GENERATED FROM
THE PVT DATA ON HELIUM OBTAINED BY MICHELS AND WOUTERS

BY

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Fundamental Research

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AND 150° C AND PRESSURES TO 300 ATMOSPHERES GENERATED FROM
THE PVT DATA ON HELIUM OBTAINED BY MICHELS AND WOUTERS

by

B. J. Dalton^{1/} and Robert E. Barieau^{2/}

ABSTRACT

The isotherms of helium published by Michels and Wouters have been reevaluated for an equation of the form

$$\left(\frac{pv}{p_o v_o}\right) = PV = \left(\frac{A_o}{T_o}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2$$

where the best values for the seven parameters were taken to be the least squares values.

From our retreatment of Michels and Wouters' data, we generated six isenthalpic curves along with compressibility factors, Joule-Thomson coefficients, relative molal heat capacities, relative molal enthalpies, and molal heat capacities.

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INTRODUCTION

The Helium Research Center is presently engaged in a critical examination of all of the PVT data on helium that appear in the literature. The long-range objective is the development of a single equation of state for helium that will allow all of the thermodynamic properties to be calculated and will reproduce all of the data within the accuracy with which the data are known. A preliminary objective is to obtain the best values of second virial coefficients and to develop an equation that will reproduce the best values as a function of temperature.

In a previous article (3)^{3/}, we evaluated second and third

3/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

virial coefficients of helium from the equation

$$(PV)_{\text{corr.}} = A_t + B(T)P + C(T)P^2 \quad (1)$$

We then represented these B's by a temperature function similar to that employed by Keyes (4).

$$B(T) = \frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}} \quad (2)$$

The B's evaluated from equation (2) represented the original B values within 0.2% or better. This was interpreted to mean that

equation (2) represented the second virials of helium for the temperature range 0° to 150° C.

We have previously shown (3) that the C's can be represented by the equation

$$C(T) = \frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}} \quad (3)$$

and that C's evaluated from equation (3) are within the limits of about one standard deviation of the original C values. This was interpreted to mean that equation (3) represented third virials within the apparent precision of the original data from which these values were determined.

Therefore, since we had what we considered to be adequate temperature functions for representing second and third virials of helium, we decided to reevaluate all of the original data reported by Michels and Wouters (6). An equation of the form

$$PV = \left(\frac{A_o}{T_o}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2 \quad (4)$$

was applied to the complete set of data where the seven unknowns: (A_o/T_o) ; b_1 ; b_2 ; b_3 ; c_1 ; c_2 ; c_3 are to be determined. The best values for the parameters appearing in equation (4) were taken to be the least squares values, each observation being assigned unit weight. Our retreatment of the original PVT data reported by Michels and Wouters is given below.

RECALCULATION OF THE ORIGINAL HELIUM ISOTHERMS REPORTED BY MICHELS AND WOUTERS

The experimental data as published by Michels and Wouters are given in table 1 of this report, the PV factors being expressed in Amagat units and the pressures in atmospheres [Amagat units are evaluated from the ratio $p_v/p_o v_o$, where p and v are the pressure and volume, respectively, at the high pressure and at some given temperature and p_o and v_o are the corresponding quantities for the same mass of gas at 0° C and 1 atmosphere]. An equation of the form

$$\left(\frac{p_v}{p_o v_o}\right) = PV = \left(\frac{A_o}{T_o}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2 \quad (4)$$

was applied to the complete set of data where the seven unknowns of equation (4) were determined. The best values for the parameters appearing in equation (4), and given in table 2 of this report, were taken to be the least squares values, each observation being assigned unit weight. The deviations given in table 2 are standard deviations. These deviations were determined by expressing each of the constants in terms of the original observations and applying the law for the "Propagation of Errors" (2, 5).

If the data reported by Michels and Wouters contained a systematic error, one would not expect PV to reduce to the reference state of the gas [the reference state is defined to be: $PV \equiv 1$ at 0° C and $P = 1$ atmosphere]. For example, suppose the high pressures were too high by some factor, say two. Then PV would reduce to two at

TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters

Pressure atm	(PV) _{exp} Michels and Wouters Amagat units	$\left[(PV)_{exp} - (PV)_{cal} \right]_{1/}$ HRC Amagat units
	Temp. = 0° C	
9.0948	1.00431	0.000041
11.2729	1.00547	0.000057
14.0727	1.00693	0.000047
17.6397	1.00876	0.000006
21.8017	1.01094	0.000005
26.7198	1.01351	0.000002
31.5272	1.01606	0.000041
35.1200	1.01790	0.000007
36.2641	1.01855	0.000060
42.6534	1.02183	0.000013
52.3285	1.02685	0.000008
64.2578	1.03303	0.000014
78.6351	1.04045	0.000023
98.010	1.05032	-0.000040
121.759	1.06245	-0.000003
152.160	1.07775	-0.000047
189.813	1.09665	0.000057
	Temp. = 25° C	
9.9266	1.09616	0.000039
12.3036	1.09740	0.000045
15.3591	1.09898	0.000040
19.2526	1.10100	0.000042
23.7946	1.10335	0.000040
29.1618	1.10614	0.000056
34.4061	1.10884	0.000049
38.3280	1.11088	0.000067
39.5749	1.11154	0.000084
46.5446	1.11505	0.000008
57.0978	1.12044	-0.000019
70.1080	1.12708	-0.000035
85.7848	1.13505	-0.000053
106.923	1.14584	0.000023
132.802	1.15881	-0.000037
165.938	1.17533	-0.000059
206.963	1.19573	0.000079

$\frac{1}{2}$ (PV)_{cal.} was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.

TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters (Con.)

Pressure atm	(PV) _{exp} Michels and Wouters Amagat units	$\left[(PV)_{\text{exp}} - (PV)_{\text{cal.}} \right]_{\text{HRC}} \frac{1}{\text{Amagat units}}$
Temp. = 50° C		
10.7582	1.18799	0.000019
13.3340	1.18930	0.000006
16.6452	1.19100	0.000007
20.8640	1.19315	-0.000006
25.7858	1.19568	0.000003
31.6005	1.19864	-0.000010
37.2837	1.20158	0.000028
41.5319	1.20374	0.000022
42.8832	1.20446	0.000053
50.4317	1.20817	-0.000079
61.8667	1.21402	-0.000034
75.9532	1.22105	-0.000132
92.9345	1.22965	-0.000089
115.820	1.24118	-0.000031
143.833	1.25507	-0.000087
179.686	1.27271	-0.000143
224.074	1.29459	0.000066
Temp. = 75° C		
11.5902	1.27986	0.000042
14.3650	1.28126	0.000030
17.9319	1.28307	0.000028
22.4766	1.28537	0.000021
27.7776	1.28804	0.000003
34.0412	1.29122	0.000012
40.1626	1.29436	0.000058
44.7368	1.29663	0.000019
46.1926	1.29741	0.000065
54.3225	1.30138	-0.000060
66.6350	1.30759	-0.000036
81.8034	1.31510	-0.000121
100.084	1.32425	-0.000083
124.722	1.33658	0.000033
154.876	1.35143	0.000041
193.458	1.37025	0.000043
241.128	1.39312	-0.000073

$\frac{1}{\text{values}}$ (PV)_{cal} was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.

TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters (Con.)

Pressure atm	(PV) _{exp} Michels and Wouters Amagat units	$\left[(PV)_{exp} - (PV)_{cal.} \right] \frac{1}{HRC}$ Amagat units
Temp. = 100° C		
12.4218	1.37170	0.000037
15.3958	1.37320	0.000038
19.2184	1.37512	0.000034
24.0889	1.37757	0.000034
29.7694	1.38040	0.000011
36.4817	1.38379	0.000035
43.0393	1.38707	0.000032
47.9414	1.38951	0.000022
49.4995	1.39029	0.000023
58.2133	1.39459	-0.000023
71.4029	1.40115	-0.000024
87.6561	1.40919	-0.000038
107.240	1.41893	0.000044
133.625	1.43199	0.000168
165.899	1.44761	0.000087
207.183	1.46747	0.000058
258.187	1.49168	-0.000001
Temp. = 125° C		
13.2532	1.46350	-0.000004
16.4261	1.46510	0.000010
20.5043	1.46713	0.000004
25.7004	1.46973	0.000014
31.7595	1.47268	-0.000053
38.9193	1.47625	-0.000041
45.9135	1.47970	-0.000061
51.1443	1.48234	-0.000011
52.8042	1.48311	-0.000063
62.0999	1.48770	-0.000066
76.1779	1.49485	0.000150
93.5026	1.50318	-0.000018
114.390	1.51354	0.000149
142.512	1.52723	0.000205
176.899	1.54360	0.000044
220.871	1.56442	-0.000049
275.189	1.58991	-0.000043

$\frac{1}{(PV)_{cal.}}$ was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.

TABLE 1. - Experimental PVT data for helium obtained by Michels and Wouters (Con.)

Pressure atm	(PV) _{exp} Michels and Wouters Amagat units	$\left[(PV)_{\text{exp}} - (PV)_{\text{cal.}} \right] \frac{1}{\text{HRC}}$ Amagat units
	Temp. = 150° C	
14.0847	1.55532	-0.000023
17.4566	1.55701	-0.000004
21.7902	1.55914	-0.000020
27.3116	1.56187	-0.000020
33.7509	1.56502	-0.000049
41.3568	1.56871	-0.000107
48.7883	1.57235	-0.000121
54.3454	1.57512	-0.000079
56.1089	1.57593	-0.000133
65.9811	1.58068	-0.000216
80.9284	1.58807	-0.000119
99.3435	1.59708	-0.000051
121.520	1.60787	0.000030
151.375	1.62221	0.000058
187.909	1.63967	0.000169
234.562	1.66139	-0.000005
292.153	1.68792	-0.000095

$\frac{1}{\text{HRC}}$ (PV)_{cal.} was evaluated from equation (4), using the least squares values for the constants given in table 2 of this report.

TABLE 2. - Virial coefficients of helium as evaluated by the Helium Research Center from the original PVT data obtained by Michels and Wouters: 0° C = 273.15° K

$$\begin{aligned}
 (A_o/T_o) &= (0.36590932 \pm 0.00000411) \times 10^{-2} \\
 b_1 &= (3.21079494 \pm 0.16219855) \times 10^{-3} \\
 b_2 &= -(2.76069068 \pm 0.60075141) \times 10^{-2} \\
 b_3 &= (1.64599720 \pm 0.55397920) \times 10^{-1} \\
 A_o &= 0.99948130 \pm 0.00001122 \\
 c_1 &= -(3.47366275 \pm 0.89251908) \times 10^{-6} \\
 c_2 &= (1.19284347 \pm 0.33335061) \times 10^{-4} \\
 c_3 &= -(1.11341304 \pm 0.31003730) \times 10^{-3}
 \end{aligned}$$

t, ° C	A_t ^{1/}	$(B \cdot 10^3)$ ^{2/}	$(-C \cdot 10^7)$ ^{3/}
0	0.999481 \pm 0.000011	0.52714 \pm 0.00061	0.8177 \pm 0.0377
25	1.090959 \pm 0.000012	0.52078 \pm 0.00042	0.7216 \pm 0.0226
50	1.182436 \pm 0.000013	0.51521 \pm 0.00041	0.6688 \pm 0.0195
75	1.273913 \pm 0.000014	0.51024 \pm 0.00040	0.6455 \pm 0.0182
100	1.365391 \pm 0.000015	0.50573 \pm 0.00038	0.6426 \pm 0.0158
125	1.456868 \pm 0.000016	0.50161 \pm 0.00038	0.6538 \pm 0.0143
150	1.548345 \pm 0.000017	0.49779 \pm 0.00045	0.6750 \pm 0.0176

^{1/} $A_t = (A_o/T_o)T$, where $T = (273.15 + t, ^\circ \text{C})$.

^{2/} Evaluated from equation (2), using the least squares values for b_1 , b_2 , and b_3 given above.

^{3/} Evaluated from equation (3), using the least squares values for c_1 , c_2 , and c_3 given above.

Since PV is not exactly equal to one, this indicates that there might be a systematic error in the data. Now in order to decide if this difference is statistically significant, we need to have an estimate of the standard error of PV at 0° C and P = 1 atm. We evaluated the standard error of our function, equation (4), at 0° C and P = 1 atm. by expressing $A_{0^{\circ}}$, $B_{0^{\circ}}$, and $C_{0^{\circ}}$ in terms of the original data and applying the law for the "Propagation of Errors" (2, 5). When we did this, we got

$$S_{(PV)} \left| \begin{array}{l} 0^{\circ} \text{ C} \\ P=1 \text{ atm.} \end{array} \right. = \pm 0.00001095$$

or

$$PV \left| \begin{array}{l} 0^{\circ} \text{ C} \\ P=1 \text{ atm.} \end{array} \right. = 1.000008 \pm 0.000011, \text{ Amagat units}$$

We see that the difference between the reference state of the gas and the PV product evaluated from equation (4) is less than a standard deviation. This is taken as statistical evidence that there is no systematic error in the experimental data reported by Michels and Wouters.

We have previously shown (3) that the temperatures as given by the primary temperature scale have smaller uncertainties than those evaluated from the PV measurements. We concluded, therefore, that

the primary scale was more accurate and that the temperature of each isotherm is as given by the primary scale. This means that we should set $A = RT$ for each isotherm, where T is evaluated from the primary temperature scale.

We reevaluated the PVT data given in reference 6 in the following way: from equation (4), for $T = T_o = 273.15^\circ \text{ K}$ and $P = 1 \text{ atm.}$, we have

$$PV \equiv 1 = \frac{A_{0^\circ}}{T_o} T_o + \left(\frac{b_1}{T_o^{1/4}} + \frac{b_2}{T_o^{3/4}} + \frac{b_3}{T_o^{5/4}} \right) + \left(\frac{c_1}{T_o^{1/4}} + \frac{c_2}{T_o^{3/4}} + \frac{c_3}{T_o^{5/4}} \right) \quad (5)$$

or,

$$A_{0^\circ} = 1 - \left(\frac{b_1}{T_o^{1/4}} + \frac{b_2}{T_o^{3/4}} + \frac{b_3}{T_o^{5/4}} \right) - \left(\frac{c_1}{T_o^{1/4}} + \frac{c_2}{T_o^{3/4}} + \frac{c_3}{T_o^{5/4}} \right) \quad (6)$$

Substituting equation (6) into equation (4), we get

$$PV = \left[\begin{aligned} & \frac{T}{T_o} + b_1 \left(\frac{P}{T^{1/4}} - \frac{T}{T_o^{5/4}} \right) + b_2 \left(\frac{P}{T^{3/4}} - \frac{T}{T_o^{7/4}} \right) \\ & + b_3 \left(\frac{P}{T^{5/4}} - \frac{T}{T_o^{9/4}} \right) + c_1 \left(\frac{P^2}{T^{1/4}} - \frac{T}{T_o^{5/4}} \right) \\ & + c_2 \left(\frac{P^2}{T^{3/4}} - \frac{T}{T_o^{7/4}} \right) + c_3 \left(\frac{P^2}{T^{5/4}} - \frac{T}{T_o^{9/4}} \right) \end{aligned} \right] \quad (7)$$

Equation (7) was then applied to the complete set of data to give the residuals given in column 3 of table 3. The parameters appearing in equation (7) were evaluated by least squares solution,

TABLE 3. - Experimental compressibility data for helium as
reevaluated using equations (6) and (7):
 $PV \equiv 1$ at $P = 1$ atm. and 0° C

Pressure atm	$(PV)_{\text{exp}}$	$[(PV)_{\text{exp}} - (PV)_{\text{cal.}}]$
	Michels and Wouters Amagat units	HRC Amagat units
Temp. = 0° C		
9.0948	1.00431	0.000048
11.2729	1.00547	0.000063
14.0727	1.00693	0.000052
17.6397	1.00876	0.000011
21.8017	1.01094	0.000010
26.7198	1.01351	0.000006
31.5272	1.01606	0.000044
35.1200	1.01790	0.000009
36.2641	1.01855	0.000062
42.6534	1.02183	0.000015
52.3285	1.02685	0.000008
64.2578	1.03303	0.000013
78.6351	1.04045	0.000021
98.010	1.05032	-0.000043
121.759	1.06245	-0.000006
152.160	1.07775	-0.000049
189.813	1.09665	0.000060
Temp. = 25° C		
9.9266	1.09616	0.000046
12.3036	1.09740	0.000052
15.3591	1.09898	0.000046
19.2526	1.10100	0.000047
23.7946	1.10335	0.000045
29.1618	1.10614	0.000059
34.4061	1.10884	0.000051
38.3280	1.11088	0.000069
39.5749	1.11154	0.000086
46.5446	1.11505	0.000009
57.0978	1.12044	-0.000019
70.1080	1.12708	-0.000037
85.7848	1.13505	-0.000056
106.923	1.14584	0.000019
132.802	1.15881	-0.000041
165.938	1.17533	-0.000061
206.963	1.19573	0.000083

TABLE 3. - Experimental compressibility data for helium as
reevaluated using equations (6) and (7):
PV \equiv 1 at P = 1 atm. and 0° C (Con.)

Pressure atm	(PV) _{exp} Michels and Wouters Amagat units	$[(PV)_{exp} - (PV)_{cal.}]$ HRC Amagat units
	Temp. = 50° C	
10.7582	1.18799	0.000027
13.3340	1.18930	0.000013
16.6452	1.19100	0.000013
20.8640	1.19315	0.000000
25.7858	1.19568	0.000008
31.6005	1.19864	-0.000006
37.2837	1.20158	0.000031
41.5319	1.20374	0.000024
42.8832	1.20446	0.000055
50.4317	1.20817	-0.000078
61.8667	1.21402	-0.000035
75.9532	1.22105	-0.000134
92.9345	1.22965	-0.000093
115.820	1.24118	-0.000035
143.833	1.25507	-0.000091
179.686	1.27271	-0.000145
224.074	1.29459	0.000071
	Temp. = 75° C	
11.5902	1.27986	0.000050
14.3650	1.28126	0.000038
17.9319	1.28307	0.000035
22.4766	1.28537	0.000027
27.7776	1.28804	0.000008
34.0412	1.29122	0.000016
40.1626	1.29436	0.000061
44.7368	1.29663	0.000022
46.1926	1.29741	0.000067
54.3225	1.30138	-0.000059
66.6350	1.30759	-0.000037
81.8034	1.31510	-0.000123
100.084	1.32425	-0.000087
124.722	1.33658	0.000028
154.876	1.35143	0.000037
193.458	1.37025	0.000041
241.128	1.39312	-0.000068

TABLE 3. - Experimental compressibility data for helium as
reevaluated using equations (6) and (7):
PV \equiv 1 at P = 1 atm. and 0° C (Con.)

Pressure atm	(PV) _{exp} Michels and Wouters Amagat units	$[(PV)_{exp} - (PV)_{cal.}]$ HRC Amagat units
	Temp. = 100° C	
12.4218	1.37170	0.000046
15.3958	1.37320	0.000047
19.2184	1.37512	0.000041
24.0889	1.37757	0.000041
29.7694	1.38040	0.000016
36.4817	1.38379	0.000039
43.0393	1.38707	0.000035
47.9414	1.38951	0.000024
49.4995	1.39029	0.000025
58.2133	1.39459	-0.000022
71.4029	1.40115	-0.000025
87.6561	1.40919	-0.000040
107.240	1.41893	0.000039
133.625	1.43199	0.000163
165.899	1.44761	0.000082
207.183	1.46747	0.000056
258.187	1.49168	0.000004
	Temp. = 125° C	
13.2532	1.46350	0.000005
16.4261	1.46510	0.000019
20.5043	1.46713	0.000012
25.7004	1.46973	0.000021
31.7595	1.47268	-0.000047
38.9193	1.47625	-0.000037
45.9135	1.47970	-0.000057
51.1443	1.48234	-0.000009
52.8042	1.48311	-0.000060
62.0999	1.48770	-0.000065
76.1779	1.49485	0.000149
93.5026	1.50318	-0.000021
114.390	1.51354	0.000144
142.512	1.52723	0.000200
176.899	1.54360	0.000039
220.871	1.56442	-0.000051
275.189	1.58991	-0.000038

TABLE 3. - Experimental compressibility data for helium as
reevaluated using equations (6) and (7):
PV \equiv 1 at P = 1 atm. and 0° C (Con.)

Pressure atm	(PV) _{exp} Michels and Wouters Amagat units	$[(PV)_{exp} - (PV)_{cal.}]$ HRC Amagat units
	Temp. = 150° C	
14.0847	1.55532	-0.000013
17.4566	1.55701	0.000005
21.7902	1.55914	-0.000012
27.3116	1.56187	-0.000013
33.7509	1.56502	-0.000043
41.3568	1.56871	-0.000102
48.7883	1.57235	-0.000117
54.3454	1.57512	-0.000076
56.1089	1.57593	-0.000131
65.9811	1.58068	-0.000215
80.9284	1.58807	-0.000120
99.3435	1.59708	-0.000054
121.520	1.60787	0.000025
151.375	1.62221	0.000053
187.909	1.63967	0.000163
234.562	1.66139	-0.000007
292.153	1.68792	-0.000090

each observation being given unit weight. These constants are given in table 4 of this report. The deviations given in table 4 are standard deviations. These deviations were evaluated by expressing each of the constants in terms of the original observations and applying the law for the "Propagation of Errors" (2, 5).

From our reevaluation of Michels and Wouters' data, we evaluated thermodynamic properties of helium for temperatures between 0° and 150° C and pressures to 300 atmospheres. Our calculations and the quantities we evaluated are given in the next section.

THERMODYNAMIC PROPERTIES OF HELIUM AS EVALUATED FROM THE RESULTS OF MICHELS AND WOUTERS' WORK

We generated six isenthalpic curves from the results of our recalculation of Michels and Wouters' PVT data on helium, corresponding to the isenthalpic zero pressure-temperature intercepts reported by Barieau and Briggs (1) in their reevaluation of Roebuck and Osterberg's Joule-Thomson data for helium. We generated these isenthalpic curves from Michels and Wouters' data in the following way. The helium isotherms reported in reference 6 were represented by the equation

$$PV = \left(\frac{A_{0^\circ}}{T_o}\right)T + \left(\frac{b_1}{T^{1/4}} + \frac{b_2}{T^{3/4}} + \frac{b_3}{T^{5/4}}\right)P + \left(\frac{c_1}{T^{1/4}} + \frac{c_2}{T^{3/4}} + \frac{c_3}{T^{5/4}}\right)P^2 \quad (8)$$

where A_{0° is defined by equation (6) and the b's and c's are the least squares values previously determined from equation (7).

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TABLE 4. - Virial coefficients for helium as calculated from equations (6) and (7)

$$\begin{aligned}
 b_1 &= (3.20923530 \pm 0.16188694) \times 10^{-3} \\
 b_2 &= -(2.74977122 \pm 0.59947520) \times 10^{-2} \\
 b_3 &= (1.63456005 \pm 0.55275691) \times 10^{-1} \\
 c_1 &= -(3.45274355 \pm 0.89045538) \times 10^{-6} \\
 c_2 &= (1.18441022 \pm 0.33255397) \times 10^{-4} \\
 c_3 &= -(1.10625748 \pm 0.30932473) \times 10^{-3}
 \end{aligned}$$

$$A_{0^\circ\text{C}} \Big|_{P=1 \text{ atm.}} = 1 - \frac{b_1}{T_o^{1/4}} - \frac{b_2}{T_o^{3/4}} - \frac{b_3}{T_o^{5/4}} - \frac{c_1}{T_o^{1/4}} - \frac{c_2}{T_o^{3/4}} - \frac{c_3}{T_o^{5/4}}$$

$t, ^\circ\text{C}$	$A_t = A_{0^\circ} \left(\frac{T}{T_o} \right)$	$(B \times 10^3)^{1/}$	$-(C \times 10^7)^{2/}$
0	0.999473	0.52735 ± 0.00054	0.8273 ± 0.0354
25	1.090949	0.52101 ± 0.00031	0.7310 ± 0.0189
50	1.182426	0.51544 ± 0.00028	0.6778 ± 0.0154
75	1.273902	0.51047 ± 0.00026	0.6541 ± 0.0142
100	1.365379	0.50597 ± 0.00022	0.6507 ± 0.0117
125	1.456855	0.50184 ± 0.00022	0.6614 ± 0.0104
150	1.548332	0.49802 ± 0.00033	0.6820 ± 0.0150

$$\underline{1/} \quad B(T) = \frac{1}{T^{1/4}} \left[b_1 + \frac{b_2}{T^{1/2}} + \frac{b_3}{T} \right]$$

$$\underline{2/} \quad C(T) = \frac{1}{T^{1/4}} \left[c_1 + \frac{c_2}{T^{1/2}} + \frac{c_3}{T} \right]$$

Note: The variances and covariances of the parameters appearing in equation (7) are given in the appendix of this report.

Dividing both sides of equation (8) by TP ,

$$\frac{V}{T} = \left(\frac{A_{0^\circ}}{T_o P}\right) + \left(\frac{b_1}{T^{5/4}} + \frac{b_2}{T^{7/4}} + \frac{b_3}{T^{9/4}}\right) + \left(\frac{c_1}{T^{5/4}} + \frac{c_2}{T^{7/4}} + \frac{c_3}{T^{9/4}}\right)P \quad (9)$$

Differentiating equation (9) with respect to $(1/T)$, keeping the pressure constant, we get

$$\left[\frac{\partial(V/T)}{\partial(1/T)}\right]_P = \frac{1}{4T^{1/4}} \left[\left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right) + \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right)P \right] \quad (10)$$

But

$$\left[\frac{\partial(V/T)}{\partial(1/T)}\right]_P = \left(\frac{\partial H}{\partial P}\right)_T \quad (11)$$

Substituting equation (11) into equation (10), we get

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{1}{4T^{1/4}} \left[\left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right) + \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right)P \right] \quad (12)$$

Integrating equation (12) from $P = 0$ to $P = P$ at constant temperature, we get

$$\left(H_P - H_{P=0}\right)_T = \frac{1}{4T^{1/4}} \left[\left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right)P + \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right)\frac{P^2}{2} \right] \quad (13)$$

We employed equation (13) and the expression

$$(\Delta H)_P = C_P^o \Delta T = \frac{5}{2} R \Delta T \quad (14)$$

to generate isenthalpic curves for helium from Michels and Wouters' data corresponding to the isenthalpic zero pressure-temperature intercepts reported in reference 1. The isenthalpic zero pressure-temperature intercepts reported by Barieau and Briggs (1) are given in table 5 of this report; the isenthalpic curves we generated from the data of Michels and Wouters, corresponding to the zero pressure-temperature intercepts of table 5, are given in table 6 of this report.

Compressibility factors for helium for temperatures between 0° and 150° C and pressures to 300 atmospheres are given in table 7 of this report. These Z's were evaluated by dividing both sides of equation (8) by the factor $(A_{0^{\circ}}/T_o)T$. When we do this, we see that Z is expressible by the equation

$$\frac{(PV)}{(A_{0^{\circ}}/T_o)T} = Z = 1 + \frac{1}{(A_{0^{\circ}}/T_o)} \left[\left(\frac{b_1}{T^{5/4}} + \frac{b_2}{T^{7/4}} + \frac{b_3}{T^{9/4}} \right) P + \left(\frac{c_1}{T^{5/4}} + \frac{c_2}{T^{7/4}} + \frac{c_3}{T^{9/4}} \right) P^2 \right] \quad (15)$$

The deviations listed in table 7 are standard deviations. These deviations were determined by expressing Z in terms of the original observations and applying the law for the "Propagation of Errors" (2, 5).

Table 8 of this report gives ρR products as a function of temperature and pressure, where ρ is the density and R is the gas constant. These ρR products were determined from the equation

$$\rho R = \frac{P}{ZT} \quad (16)$$

TABLE 5. - Isenthalpic zero pressure-temperature intercepts reported by Briggs and Barieau in their recalculation of Roebuck and Osterberg's μ data for helium for temperatures between 0° and 150° C

Curve	<u>Zero Pressure-Temperature Intercept</u>	
	° C	° K
150	165.414	438.564
100	113.099	386.249
75	88.214	361.364
50	63.789	336.939
25	36.770	309.920
0	12.141	285.291

TABLE 6. - Isenthalpic curves generated from the PVT data on helium obtained by
Michels and Wouters

<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>
438.564	0.0000	386.249	0.0000	361.364	0.0000
438	9.2506	386	4.0150	361	5.8132
437	25.6527	385	20.1462	360	21.7957
436	42.0560	384	36.2888	359	37.7973
435	58.4609	383	52.4438	358	53.8193
434	74.8678	382	68.6122	357	69.8631
433	91.2774	381	84.7951	356	85.9301
432	107.6903	380	100.9934	355	102.0217
431	124.1069	379	117.2084	354	118.1395
430	140.5279	378	133.4411	353	134.2850
429	156.9539	377	149.6927	352	150.4599
428	173.3854	376	165.9644	351	166.6659
427	189.8233	375	182.2575	350	182.9046
426	206.2681	374	198.5733	349	199.1780
425	222.7204	373	214.9131	348	215.4878
424	239.1811	372	231.2783	347	231.8361
423	255.6508	371	247.6704	346	248.2249
422	272.1303	370	264.0907	345	264.6563
421	288.6203	369	280.5409	344	281.1324
420	305.1217	368	297.0224	343	297.6557

TABLE 6. - Isenthalpic curves generated from the PVT data on helium obtained by Michels and Wouters (Con.)

<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>	<u>T</u> <u>°K</u>	<u>P</u> <u>atm</u>
336.939	0.0000	309.920	0.0000	285.291	0.0000
336	14.8420	309	14.3429	285	4.4646
335	30.6751	308	29.9722	284	19.8419
334	46.5379	307	45.6449	283	35.2764
333	62.4320	306	61.3635	282	50.7715
332	78.3594	305	77.1307	281	66.3309
331	94.3221	304	92.9493	280	81.9584
330	110.3221	303	108.8224	279	97.6582
329	126.3616	302	124.7530	278	113.4345
328	142.4427	301	140.7444	277	129.2919
327	158.5679	300	156.8001	276	145.2353
326	174.7395	299	172.9234	275	161.2697
325	190.9600	298	189.1184	274	177.4005
324	207.2321	297	205.3889	273	193.6335
323	223.5585	296	221.7390	272	209.9747
322	239.9421	295	238.1732	271	226.4307
321	256.3858	294	254.6961	270	243.0083
320	272.8927	293	271.3126	269	259.7150
319	289.4662	292	288.0278	268	276.5585
318	306.1096	291	304.8472	267	293.5472

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TABLE 7. - Compressibility factors of helium: $Z = P/\rho RT$

<u>T, ° K</u>	<u>P,atm. 0</u>	<u>P,atm. 1</u>	<u>P,atm. 5</u>
273.15	1.0000000	1.0005275 \pm 0.0000005	1.0026361 \pm 0.0000026
275	1.0000000	1.0005235 \pm 0.0000005	1.0026159 \pm 0.0000025
300	1.0000000	1.0004742 \pm 0.0000003	1.0023695 \pm 0.0000013
325	1.0000000	1.0004331 \pm 0.0000002	1.0021641 \pm 0.0000011
350	1.0000000	1.0003983 \pm 0.0000002	1.0019903 \pm 0.0000010
375	1.0000000	1.0003685 \pm 0.0000002	1.0018414 \pm 0.0000008
400	1.0000000	1.0003426 \pm 0.0000002	1.0017122 \pm 0.0000008
425	1.0000000	1.0003200 \pm 0.0000002	1.0015993 \pm 0.0000011

TABLE 7. - Compressibility factors of helium: $Z = P/\rho RT$ (Con.)

<u>T, ° K</u>	P,atm. <u>10</u>	P,atm. <u>20</u>	P,atm. <u>50</u>
273.15	1.0052680 \pm 0.0000051	1.0105194 \pm 0.0000095	1.0261744 \pm 0.0000190
275	1.0052277 \pm 0.0000048	1.0104390 \pm 0.0000089	1.0259756 \pm 0.0000178
300	1.0047357 \pm 0.0000026	1.0094581 \pm 0.0000048	1.0235462 \pm 0.0000098
325	1.0043254 \pm 0.0000022	1.0086395 \pm 0.0000042	1.0215137 \pm 0.0000088
350	1.0039781 \pm 0.0000019	1.0079461 \pm 0.0000036	1.0197887 \pm 0.0000076
375	1.0036804 \pm 0.0000015	1.0073512 \pm 0.0000028	1.0183069 \pm 0.0000060
400	1.0034222 \pm 0.0000015	1.0068354 \pm 0.0000028	1.0170206 \pm 0.0000060
425	1.0031964 \pm 0.0000021	1.0063839 \pm 0.0000040	1.0158939 \pm 0.0000086

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TABLE 7. - Compressibility factors of helium: $Z = P/\rho RT$ (Con.)

<u>T, ° K</u>	P,atm. <u>75</u>	P,atm. <u>100</u>	P,atm. <u>150</u>
273.15	1.0391064 \pm 0.0000229	1.0519349 \pm 0.0000242	1.0772815 \pm 0.0000285
275	1.0388110 \pm 0.0000215	1.0515446 \pm 0.0000227	1.0767070 \pm 0.0000267
300	1.0351953 \pm 0.0000121	1.0467618 \pm 0.0000129	1.0696468 \pm 0.0000142
325	1.0321641 \pm 0.0000111	1.0427435 \pm 0.0000122	1.0636893 \pm 0.0000130
350	1.0295874 \pm 0.0000096	1.0393224 \pm 0.0000107	1.0586010 \pm 0.0000114
375	1.0273713 \pm 0.0000076	1.0363765 \pm 0.0000086	1.0542089 \pm 0.0000092
400	1.0254460 \pm 0.0000079	1.0338148 \pm 0.0000090	1.0503826 \pm 0.0000098
425	1.0237584 \pm 0.0000113	1.0315679 \pm 0.0000129	1.0470221 \pm 0.0000141

TABLE 7. - Compressibility factors of helium: $Z = P/\rho RT$ (Con.)

<u>T, ° K</u>	<u>P,atm. 200</u>	<u>P,atm. 250</u>	<u>P,atm. 300</u>
273.15	1.1022142 \pm 0.0000554	1.1267331 \pm 0.0001061	1.1508381 \pm 0.0001765
275	1.1014628 \pm 0.0000520	1.1258120 \pm 0.0000998	1.1497545 \pm 0.0001662
300	1.0922011 \pm 0.0000247	1.1144249 \pm 0.0000471	1.1363180 \pm 0.0000793
325	1.0843513 \pm 0.0000183	1.1047295 \pm 0.0000332	1.1248237 \pm 0.0000563
350	1.0776246 \pm 0.0000158	1.0963932 \pm 0.0000282	1.1149067 \pm 0.0000476
375	1.0718041 \pm 0.0000122	1.0891620 \pm 0.0000211	1.1062827 \pm 0.0000356
400	1.0667241 \pm 0.0000109	1.0828392 \pm 0.0000163	1.0987280 \pm 0.0000271
425	1.0622564 \pm 0.0000154	1.0772708 \pm 0.0000224	1.0920654 \pm 0.0000370

TABLE 8. - Values of ρR , atm/° K

<u>T, ° K</u>	<u>P, atm. 0</u>	<u>P, atm. 1</u>	<u>P, atm. 5</u>	<u>P, atm. 10</u>
273.15	0	0.00365906	0.01825683	0.03641807
275	0	0.00363446	0.01813438	0.03617453
300	0	0.00333175	0.01662727	0.03317622
325	0	0.00307559	0.01535139	0.03063671
350	0	0.00285601	0.01425734	0.02845822
375	0	0.00266568	0.01330883	0.02656888
400	0	0.00249914	0.01247863	0.02491474
425	0	0.00235219	0.01174592	0.02345444

TABLE 8. - Values of ρR , atm/ $^{\circ}$ K (Con.)

<u>T, $^{\circ}$ K</u>	<u>P, atm. 20</u>	<u>P, atm. 50</u>	<u>P, atm. 75</u>	<u>P, atm. 100</u>
273.15	0.07245763	0.17838061	0.26424091	0.34802460
275	0.07197591	0.17721491	0.26253792	0.34581163
300	0.06604203	0.16283258	0.24150032	0.31844240
325	0.06101135	0.15060606	0.22357805	0.29507959
350	0.05669237	0.14008504	0.20812775	0.27490439
375	0.05294413	0.13093630	0.19467158	0.25730675
400	0.04966055	0.12290803	0.18284727	0.24182281
425	0.04676031	0.11580645	0.17237523	0.22809368

TABLE 8. - Values of ρR , atm/ $^{\circ}$ K (Con.)

<u>T, $^{\circ}$ K</u>	<u>P, atm. 150</u>	<u>P, atm. 200</u>	<u>P, atm. 250</u>	<u>P, atm. 300</u>
273.15	0.50975425	0.66429774	0.81230242	0.95434591
275	0.50659513	0.66027896	0.80749799	0.94881913
300	0.46744404	0.61038819	0.74776985	0.88003530
325	0.43390343	0.56751404	0.69630693	0.82064145
350	0.40484698	0.53026681	0.65148682	0.76880230
375	0.37943144	0.49760339	0.61209138	0.72314248
400	0.35701276	0.46872476	0.57718634	0.68260755
425	0.33709049	0.44300816	0.54604216	0.64637368

where P is the pressure in atmospheres, T is the temperature in $^{\circ}$ K, and Z is the compressibility factor of helium corresponding to a given P and T .

If we divide both sides of equation (13) by R , where $R = (A_{0^{\circ}}/T_o)$, then we get an expression from which we can evaluate relative enthalpies, L/R . That is,

$$\left(\frac{H_P - H_{P=0}}{R}\right)_T = \left(\frac{L}{R}\right)_T = \frac{1}{4(A_{0^{\circ}}/T_o)T^{1/4}} \left[\left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T}\right)P + \left(5c_1 + \frac{7c_2}{T^{1/2}} + \frac{9c_3}{T}\right)\frac{P^2}{2} \right] \quad (17)$$

Relative enthalpies are given in table 9 of this report for temperatures between 0° and 150° C and pressures to 300 atmospheres along with the standard deviation of each of these values.

If we differentiate equation (17) with regard to the temperature, keeping the pressure constant, we get an expression of the form

$$\frac{\left[d(H_P - H_{P=0})/dT\right]_P}{R} = \left(\frac{C_P - C_P^o}{R}\right) = -\frac{1}{16(A_{0^{\circ}}/T_o)T^{5/4}} \left[\left(5b_1 + \frac{21b_2}{T^{1/2}} + \frac{45b_3}{T}\right)P + \left(5c_1 + \frac{21c_2}{T^{1/2}} + \frac{45c_3}{T}\right)\frac{P^2}{2} \right] \quad (18)$$

TABLE 9. - Values of relative enthalpies, $\frac{H_P - H_{P=0}}{R} = \frac{L}{R}, ^\circ K$

<u>T, ° K</u>	<u>P, atm. 0</u>	<u>P, atm. 1</u>	<u>P, atm. 5</u>	<u>P, atm. 10</u>
273.15	0	0.164 ± 0.002	0.822 ± 0.008	1.642 ± 0.016
275	0	0.164 ± 0.002	0.820 ± 0.008	1.639 ± 0.015
300	0	0.161 ± 0.001	0.807 ± 0.004	1.613 ± 0.008
325	0	0.159 ± 0.000	0.796 ± 0.002	1.591 ± 0.004
350	0	0.157 ± 0.000	0.786 ± 0.002	1.572 ± 0.004
375	0	0.156 ± 0.001	0.778 ± 0.003	1.556 ± 0.006
400	0	0.154 ± 0.001	0.771 ± 0.004	1.542 ± 0.007
425	0	0.153 ± 0.001	0.765 ± 0.004	1.530 ± 0.009

TABLE 9. - Values of relative enthalpies, $\frac{H_P - H_{P=0}}{R} = \frac{L}{R}, ^\circ \text{K}$ (Con.)

<u>T, ° K</u>	<u>P,atm. 20</u>	<u>P,atm. 50</u>	<u>P,atm. 75</u>	<u>P,atm. 100</u>
273.15	3.277 ± 0.031	8.148 ± 0.070	12.166 ± 0.097	16.147 ± 0.118
275	3.273 ± 0.030	8.139 ± 0.067	12.153 ± 0.093	16.132 ± 0.114
300	3.221 ± 0.016	8.021 ± 0.037	11.992 ± 0.051	15.937 ± 0.062
325	3.179 ± 0.008	7.923 ± 0.019	11.856 ± 0.026	15.770 ± 0.032
350	3.142 ± 0.008	7.839 ± 0.018	11.739 ± 0.025	15.624 ± 0.031
375	3.111 ± 0.011	7.766 ± 0.025	11.635 ± 0.036	15.494 ± 0.044
400	3.084 ± 0.014	7.702 ± 0.033	11.542 ± 0.046	15.376 ± 0.057
425	3.060 ± 0.017	7.643 ± 0.039	11.459 ± 0.054	15.269 ± 0.067

TABLE 9. - Values of relative enthalpies, $\frac{H_P - H_{P=0}}{R} = \frac{L}{R}$, ° K (Con.)

<u>T, ° K</u>	<u>P,atm. 150</u>	<u>P,atm. 200</u>	<u>P,atm. 250</u>	<u>P,atm. 300</u>
273.15	23.997 ± 0.147	31.698 ± 0.161	39.250 ± 0.168	46.653 ± 0.184
275	23.979 ± 0.141	31.681 ± 0.154	39.237 ± 0.161	46.647 ± 0.177
300	23.746 ± 0.076	31.449 ± 0.082	39.047 ± 0.085	46.53Y ± 0.095
325	23.540 ± 0.038	31.233 ± 0.041	38.849 ± 0.042	46.388 ± 0.048
350	23.353 ± 0.039	31.028 ± 0.044	38.647 ± 0.046	46.211 ± 0.048
375	23.183 ± 0.057	30.833 ± 0.065	38.444 ± 0.068	46.016 ± 0.070
400	23.025 ± 0.073	30.646 ± 0.083	38.241 ± 0.087	45.809 ± 0.090
425	22.877 ± 0.086	30.467 ± 0.096	38.039 ± 0.101	45.593 ± 0.105

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210	1211	1212	1213	1214	1215	1216	1217	1218	1219	1220	1221	12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from which the relative molal heat capacities listed in table 10 were calculated. The deviations given in table 10 are standard deviations.

Suppose we rearrange equation (18), substituting $C_P^O(\text{He}) = 5/2 R$. When we do this, we get the following expression:

$$\frac{C_P}{R} = 2.5 - \frac{1}{16(A_{0^{\circ}}/T_0)T^{5/4}} \left[\left(5b_1 + \frac{21b_2}{T^{1/2}} + \frac{45b_3}{T} \right)P + \left(5c_1 + \frac{21c_2}{T^{1/2}} + \frac{45c_3}{T} \right) \frac{P^2}{2} \right] \quad (19)$$

from which the molal heat capacity values given in table 11 of this report were calculated. The deviations given in table 11 are standard deviations.

Joule-Thomson coefficients for helium at zero pressure for temperatures between 0° and 150° C were calculated as follows. $\mu_{P=0}$ is defined by the equation

$$\mu_{P=0} = \left[\left(\frac{dT}{dP} \right)_H \right]_{P=0} = - \frac{\left[(\partial H / \partial P)_T \right]_{P=0}}{\left[(\partial H / \partial T)_P \right]_{P=0}} \quad (20)$$

But $\left[(\partial H / \partial T)_P \right]_{P=0} = C_P^O$ and C_P^O for helium $= 2.5 R$. Therefore,

$$\mu_{P=0} = - \frac{\left[(\partial H / \partial P)_T \right]_{P=0}}{C_P^O} = - \frac{\left[(\partial H / \partial P)_T \right]_{P=0}}{2.5 R} \quad (21)$$

We have previously shown that $(\partial H / \partial P)_T$ is expressible by equation (12). Substituting equation (12) into equation (21), $\mu_{P=0}$ is

TABLE 10. - Values of relative molal heat capacities, $\frac{C_P - C_{P=0}}{R} = \frac{J}{R}$

<u>T, ° K</u>	<u>P, atm.</u> <u>0</u>	<u>P, atm.</u> <u>1</u>	<u>P, atm.</u> <u>5</u>	<u>P, atm.</u> <u>10</u>
273.15	0	-0.0001 ± 0.0000	-0.0006 ± 0.0002	-0.0012 ± 0.0003
275	0	-0.0001 ± 0.0000	-0.0006 ± 0.0002	-0.0012 ± 0.0003
300	0	-0.0001 ± 0.0000	-0.0005 ± 0.0001	-0.0010 ± 0.0002
325	0	-0.0001 ± 0.0000	-0.0004 ± 0.0001	-0.0008 ± 0.0002
350	0	-0.0001 ± 0.0000	-0.0003 ± 0.0001	-0.0007 ± 0.0001
375	0	-0.0001 ± 0.0000	-0.0003 ± 0.0000	-0.0006 ± 0.0001
400	0	-0.0001 ± 0.0000	-0.0003 ± 0.0000	-0.0005 ± 0.0001
425	0	-0.0000 ± 0.0000	-0.0002 ± 0.0000	-0.0005 ± 0.0000

TABLE 10. - Values of relative molal heat capacities, $\frac{C_P - C_{P=0}}{R} = \frac{J}{R}$ (Con.)

<u>T, ° K</u>	<u>P, atm. 20</u>	<u>P, atm. 50</u>	<u>P, atm. 75</u>	<u>P, atm. 100</u>
273.15	-0.0023 ± 0.0007	-0.0052 ± 0.0015	-0.0071 ± 0.0021	-0.0086 ± 0.0026
275	-0.0023 ± 0.0007	-0.0052 ± 0.0015	-0.0070 ± 0.0021	-0.0085 ± 0.0026
300	-0.0019 ± 0.0005	-0.0043 ± 0.0011	-0.0059 ± 0.0015	-0.0072 ± 0.0019
325	-0.0016 ± 0.0003	-0.0036 ± 0.0008	-0.0050 ± 0.0011	-0.0062 ± 0.0014
350	-0.0013 ± 0.0003	-0.0031 ± 0.0006	-0.0044 ± 0.0008	-0.0055 ± 0.0010
375	-0.0012 ± 0.0002	-0.0027 ± 0.0004	-0.0039 ± 0.0006	-0.0049 ± 0.0007
400	-0.0010 ± 0.0001	-0.0024 ± 0.0003	-0.0035 ± 0.0004	-0.0045 ± 0.0005
425	-0.0009 ± 0.0001	-0.0022 ± 0.0002	-0.0032 ± 0.0003	-0.0041 ± 0.0004

TABLE 10. - Values of relative molal heat capacities, $\frac{C_P - C_{P=0}}{R} = \frac{J}{R}$ (Con.)

<u>T, ° K</u>	<u>P, atm. 150</u>	<u>P, atm. 200</u>	<u>P, atm. 250</u>	<u>P, atm. 300</u>
273.15	-0.0101 ± 0.0033	-0.0096 ± 0.0037	-0.0073 ± 0.0039	-0.0031 ± 0.0041
275	-0.0100 ± 0.0033	-0.0096 ± 0.0036	-0.0074 ± 0.0038	-0.0033 ± 0.0040
300	-0.0087 ± 0.0024	-0.0089 ± 0.0026	-0.0078 ± 0.0027	-0.0053 ± 0.0029
325	-0.0078 ± 0.0017	-0.0084 ± 0.0019	-0.0080 ± 0.0020	-0.0066 ± 0.0021
350	-0.0071 ± 0.0013	-0.0080 ± 0.0014	-0.0081 ± 0.0015	-0.0075 ± 0.0016
375	-0.0066 ± 0.0009	-0.0076 ± 0.0010	-0.0081 ± 0.0011	-0.0081 ± 0.0011
400	-0.0061 ± 0.0007	-0.0073 ± 0.0007	-0.0081 ± 0.0008	-0.0085 ± 0.0008
425	-0.0057 ± 0.0005	-0.0070 ± 0.0005	-0.0080 ± 0.0005	-0.0087 ± 0.0006

TABLE 11. - Values of molal heat capacities, $\frac{C_P}{R}$

<u>T, ° K</u>	<u>P, atm. 0</u>	<u>P, atm. 1</u>	<u>P, atm. 5</u>	<u>P, atm. 10</u>
273.15	2.5000	2.4999 \pm 0.0000	2.4994 \pm 0.0002	2.4988 \pm 0.0003
275	2.5000	2.4999 \pm 0.0000	2.4994 \pm 0.0002	2.4988 \pm 0.0003
300	2.5000	2.4999 \pm 0.0000	2.4995 \pm 0.0001	2.4990 \pm 0.0002
325	2.5000	2.4999 \pm 0.0000	2.4996 \pm 0.0001	2.4992 \pm 0.0002
350	2.5000	2.4999 \pm 0.0000	2.4997 \pm 0.0001	2.4993 \pm 0.0001
375	2.5000	2.4999 \pm 0.0000	2.4997 \pm 0.0000	2.4994 \pm 0.0001
400	2.5000	2.4999 \pm 0.0000	2.4997 \pm 0.0000	2.4995 \pm 0.0001
425	2.5000	2.5000 \pm 0.0000	2.4998 \pm 0.0000	2.4995 \pm 0.0000

TABLE 11. - Values of molal heat capacities, $\frac{C_P}{R}$ (Con.)

<u>T, ° K</u>	<u>P, atm. 20</u>	<u>P, atm. 50</u>	<u>P, atm. 75</u>	<u>P, atm. 100</u>
273.15	2.4977 ± 0.0007	2.4948 ± 0.0015	2.4929 ± 0.0021	2.4914 ± 0.0026
275	2.4977 ± 0.0007	2.4948 ± 0.0015	2.4930 ± 0.0021	2.4915 ± 0.0026
300	2.4981 ± 0.0005	2.4957 ± 0.0011	2.4941 ± 0.0015	2.4928 ± 0.0019
325	2.4984 ± 0.0003	2.4964 ± 0.0008	2.4950 ± 0.0011	2.4938 ± 0.0014
350	2.4987 ± 0.0003	2.4969 ± 0.0006	2.4956 ± 0.0008	2.4945 ± 0.0010
375	2.4988 ± 0.0002	2.4973 ± 0.0004	2.4961 ± 0.0006	2.4951 ± 0.0007
400	2.4990 ± 0.0001	2.4976 ± 0.0003	2.4965 ± 0.0004	2.4955 ± 0.0005
425	2.4991 ± 0.0001	2.4978 ± 0.0002	2.4968 ± 0.0003	2.4959 ± 0.0004

TABLE 11. - Values of molal heat capacities, $\frac{C_P}{R}$ (Con.)

<u>T, ° K</u>	<u>P, atm. 150</u>	<u>P, atm. 200</u>	<u>P, atm. 250</u>	<u>P, atm. 300</u>
273.15	2.4899 ± 0.0033	2.4904 ± 0.0037	2.4927 ± 0.0039	2.4969 ± 0.0041
275	2.4900 ± 0.0033	2.4904 ± 0.0036	2.4926 ± 0.0038	2.4967 ± 0.0040
300	2.4913 ± 0.0024	2.4911 ± 0.0026	2.4922 ± 0.0027	2.4947 ± 0.0029
325	2.4922 ± 0.0017	2.4916 ± 0.0019	2.4920 ± 0.0020	2.4934 ± 0.0021
350	2.4929 ± 0.0013	2.4920 ± 0.0014	2.4919 ± 0.0015	2.4925 ± 0.0016
375	2.4934 ± 0.0009	2.4924 ± 0.0010	2.4919 ± 0.0011	2.4919 ± 0.0011
400	2.4939 ± 0.0007	2.4927 ± 0.0007	2.4919 ± 0.0008	2.4915 ± 0.0008
425	2.4943 ± 0.0005	2.4930 ± 0.0005	2.4920 ± 0.0005	2.4913 ± 0.0006

expressible as

$$\mu_{P=0} = - \frac{1}{4T^{1/4}(2.5R)} \left(5b_1 + \frac{7b_2}{T^{1/2}} + \frac{9b_3}{T} \right) \quad (22)$$

where $R = (A_{0^\circ}/T_o)$. We employed equation (22) in evaluating the $\mu_{P=0}$ values for helium given in column 4 of table 12. The standard deviations of the $\mu_{P=0}$ values calculated from equation (22) are also given in this table. These standard deviations were evaluated by expressing $\mu_{P=0}$ in terms of the original data and applying the law for the "Propagation of Errors" (2, 5).

TABLE 12. - Joule-Thomson coefficients calculated from the original PVT data on helium obtained by Michels and Wouters

Curve	Zero Pressure-Temperature Intercept		$[(-\mu \times 10^2)_{P=0}]$
° C	° K	° C	° K/atm.
	273.150	0.000	6.578 ± 0.065
	275.000	1.850	6.569 ± 0.063
0	285.291	<u>1/</u> 12.141	6.521 ± 0.050
	300.000	26.850	6.460 ± 0.035
25	309.920	<u>1/</u> 36.770	6.422 ± 0.027
	325.000	51.850	6.369 ± 0.018
50	336.939	<u>1/</u> 63.789	6.332 ± 0.015
	350.000	76.850	6.294 ± 0.016
75	361.364	<u>1/</u> 88.214	6.263 ± 0.019
	375.000	101.850	6.229 ± 0.023
100	386.249	<u>1/</u> 113.099	6.202 ± 0.026
	400.000	126.850	6.172 ± 0.030
	425.000	151.850	6.122 ± 0.035
150	438.564	<u>1/</u> 165.414	6.097 ± 0.037

1/ Values reported in reference 1 for the average zero pressure-temperature intercept.

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APPENDIX

The variances and covariances of the parameters appearing in equation (7) are

$$s_{b_1}^2 = 2.62073816 \times 10^{-8}$$

$$s_{b_2}^2 = 3.59370510 \times 10^{-5}$$

$$s_{b_3}^2 = 3.05540196 \times 10^{-3}$$

$$s_{c_1}^2 = 7.92910782 \times 10^{-13}$$

$$s_{c_2}^2 = 1.10592146 \times 10^{-9}$$

$$s_{c_3}^2 = 9.56817913 \times 10^{-8}$$

$$s_{b_1 b_2}^2 = -9.69954948 \times 10^{-7}$$

$$s_{b_1 b_3}^2 = 8.92894480 \times 10^{-6}$$

$$s_{b_1 c_1}^2 = -1.33199188 \times 10^{-10}$$

$$s_{b_1 c_2}^2 = 4.95015561 \times 10^{-9}$$

$$s_{b_1 c_3}^2 = -4.57577779 \times 10^{-8}$$

$$s_{b_2 b_3}^2 = -3.31177972 \times 10^{-4}$$

$$s_{b_2 c_1}^2 = 4.95085186 \times 10^{-9}$$

$$s_{b_2 c_2}^2 = -1.84191718 \times 10^{-7}$$

$$s_{b_2 c_3}^2 = 1.70451669 \times 10^{-6}$$

$$s_{b_3 c_1}^2 = -4.57756903 \times 10^{-8}$$

$$s_{b_3 c_2}^2 = 1.70495217 \times 10^{-6}$$

$$s_{b_3 c_3}^2 = -1.57961978 \times 10^{-5}$$

$$s_{c_1 c_2}^2 = -2.95963973 \times 10^{-11}$$

$$s_{c_1 c_3}^2 = 2.74817895 \times 10^{-10}$$

$$s_{c_2 c_3}^2 = -1.02806132 \times 10^{-8}$$

The above quantities were determined by expressing each constant in terms of the original observations and applying the law for the "Propagation of Errors." The standard deviation in any other calculated thermodynamic quantity evaluated from equation (8) can be determined from these variances and covariances.

